

the tip. A nanotube that is one graphitic layer thick has not been observed before, although the properties of such tubes have been the subject of much speculation<sup>13</sup>. Preparing single-layer nanotubes by the selective oxidation method described here may enable these predictions to be tested. We also measured the surface areas of the bulk samples before and after carbon dioxide treatments and found that surface areas increased from 21.0 to 31.7 m<sup>2</sup> g<sup>-1</sup>.

In our experiments we use the mild oxidizing agent carbon dioxide, and the chemical reaction which occurs is



This reverse Boudouard reaction is thermodynamically favour-

able with the equilibrium constant  $K_p$  of 1.76 at our reaction temperature<sup>14</sup>, although the equilibrium constant of entirely closed graphite tubes is likely to be slightly different from other types of carbon.

Our observations indicate that the more reactive outer carbon layers at the tip of the cap selectively react with carbon dioxide and are subsequently stripped off. The selective attack of the curved part of a cap reflects greater reactivity which may be due to greater strain and the presence of pentagonal rings<sup>7</sup>. Destruction of the cap exposes the terminated cylinder layers which can then be further eroded to form thinner tubes. The observed increase in surface area may be explained by a combination of a reduction in the average tube diameter and the removal of caps from some of the nanotubes. □

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## Opening carbon nanotubes with oxygen and implications for filling

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CAPPED hollow carbon nanotubes<sup>1,2</sup> can be modified into nanocomposite fibres by simultaneous opening of the caps (by heating in the presence of air and lead metal) and filling of the interior with an inorganic phase<sup>3</sup>. To generalize this approach, greater understanding is needed of the reaction mechanism between the tube caps and oxygen. Here we report that the oxidation of carbon nanotubes in air for short durations above about 700 °C results in the etching away of the tube caps and the thinning of tubes through layer-by-layer peeling of the outer layers, starting from the cap region. The oxidation reaction follows an Arrhenius-

type relation with an activation energy barrier of about 225 kJ mol<sup>-1</sup> in air. Heating of closed nanotubes with an oxide (Pb<sub>3</sub>O<sub>4</sub>) in an inert atmosphere lowers the activation barrier for the reaction and opening of the tubes occurs at lower temperatures. Contrary to intuition, however, open tubes are much more difficult to fill with inorganic materials than in the one-step filling of tubes reported previously<sup>3</sup>. But various other experiments might be possible in the inner nano-cavities of the open tubes such as studies of catalysis and of low-dimensional chemistry and physics.

The experiments were done with carbon nanotubes produced by the arc-discharge method described previously<sup>2</sup>. Weighed amounts of the carbon nanotube samples were heated in air in an open quartz vessel. The samples started to show substantial loss of weight once they were heated above 700 °C. At ~850 °C the entire sample disappeared when heated for ~15 minutes. Figure 1 shows the plots corresponding to the weight-loss measurements at various temperatures for a given time period. As seen in the case of high-grade carbon fibres<sup>4</sup>, carbon nanotubes show a fairly high resistance to oxidation (negligible weight loss) up to some critical temperature (700 °C in air),

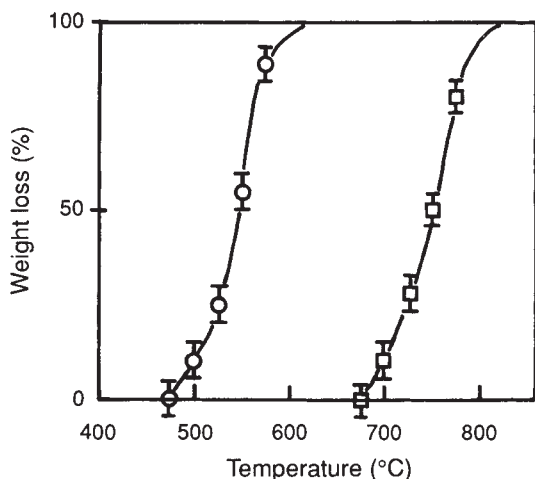


FIG. 1 Percentage weight loss of C<sub>60</sub> (circles) and nanotube/nanoparticle mixture (squares) as a function of temperature of baking in air for a given time period (15 minutes).

above which oxidation proceeds rapidly. The oxidation process follows the Arrhenius relation for temperature dependence from which we find an activation energy barrier of  $\sim 225 \text{ kJ mol}^{-1}$  in air.  $\text{C}_{60}$  is consumed in air at much lower temperatures ( $\sim 500^\circ\text{C}$ ) than the carbon nanotubes, as can be seen in Fig. 1. Despite the wide distribution in shapes and sizes of nanotubes, the oxidation curves are smooth (no steps or double peaks) over the temperature range we measured, much like that of pure  $\text{C}_{60}$ .

The state of the oxidized samples was surveyed using a transmission electron microscope, revealing that the oxidation reaction occurs preferentially at the tips of the tubes, as seen from the low-magnification image of Fig. 2. More than  $\sim 20\%$  of the tubes seen are completely open for a specimen heated in air at  $800^\circ\text{C}$  for 10 minutes. This percentage might change with the quality of the sample (average size of the nanotubes and ratio of nanoparticles) and the actual availability of oxygen to the sample. Nanoparticles are also seen to be attacked by oxygen with the removal of layers from the surface, but they seem to be much more stable than the tube caps (see Fig. 2). Even for tubes that are not completely open, peeling of the outer layers has occurred, initiating at the capped ends of the tubes (Fig. 3a). This peeling results in the thinning of the tubes layer by layer and seems to be just the reverse of the layer-by-layer growth mechanism that we have proposed<sup>5</sup>. An extreme example of this thinning from the cap to the bottom of tubes is shown in Fig. 3b, where a large tube has been opened at the tip and massively eroded from the edges. The opening of the tubes should also increase the total surface area of the sample by exposing the inside surfaces of the tubes. Figure 3c shows an opened tube, and it is evident that when tube caps open up, carbonaceous debris is sucked in (compare with the empty hollow in Fig. 3a).

From the observations, it is clear that the oxidation of the tube caps occurs at a temperature which is higher than the reaction temperature of  $\text{C}_{60}$  but lower than the temperature at which the graphite basal planes react and are consumed. Con-

sidering that the caps of the tubes react first, both the strain at the tip and the presence of pentagons might help to initiation of the oxidation process. It is known from the synthesis of  $\text{C}_{60}$  derivatives that the pyracylene moieties involving two pentagon rings is important for the chemical reactivity of  $\text{C}_{60}$  (ref. 6). In nanotubes, however, the pentagons are generally not close enough to form pyracylene units. Furthermore, nanoparticles oxidize much less readily although they have the same number of pentagons as nanotubes (12, by Euler's rule). The difference between nanoparticles and nanotube tips is only in the degree of curvature, and thus the strain. So although pentagons might play a role, strain must be the key factor in the onset of oxidation at the nanotube tips.

Intuitively one would expect that with the tube ends open it would be much easier to introduce low-melting-point materials and even pure metals, by heating in vacuum. But in fact it was very difficult to fill the open tubes with another material. When open tubes were heated in the presence of liquid lead in vacuum or an inert gas atmosphere, the outer peripheries of the open tube ends seem (from the contrast) to become decorated with a metallic phase, but no filling was observed (see Fig. 4a) despite repeated attempts under different conditions.

Previous experiments with lead metal in air<sup>3</sup> indicated that opening of tubes could occur at much lower temperatures ( $\sim 400^\circ\text{C}$ ). As we have shown here that nanotubes open only at much higher temperatures, the reactions in the case of Pb must have been catalysed either by lead particles or some form of lead oxide. To verify this we heated carbon nanotubes with  $\text{Pb}_3\text{O}_4$  (red lead) in an argon atmosphere above the melting point of the oxide ( $600^\circ\text{C}$ ). It was seen that a few of the tube tips opened up and were filled with lead material (Fig. 4b). Powder diffraction data from the heated material suggest that red lead had been changed to the lower oxide (PbO) and pure lead metal. Again the onset of the oxidation reaction shifted to lower temperature, perhaps because of the close contact with

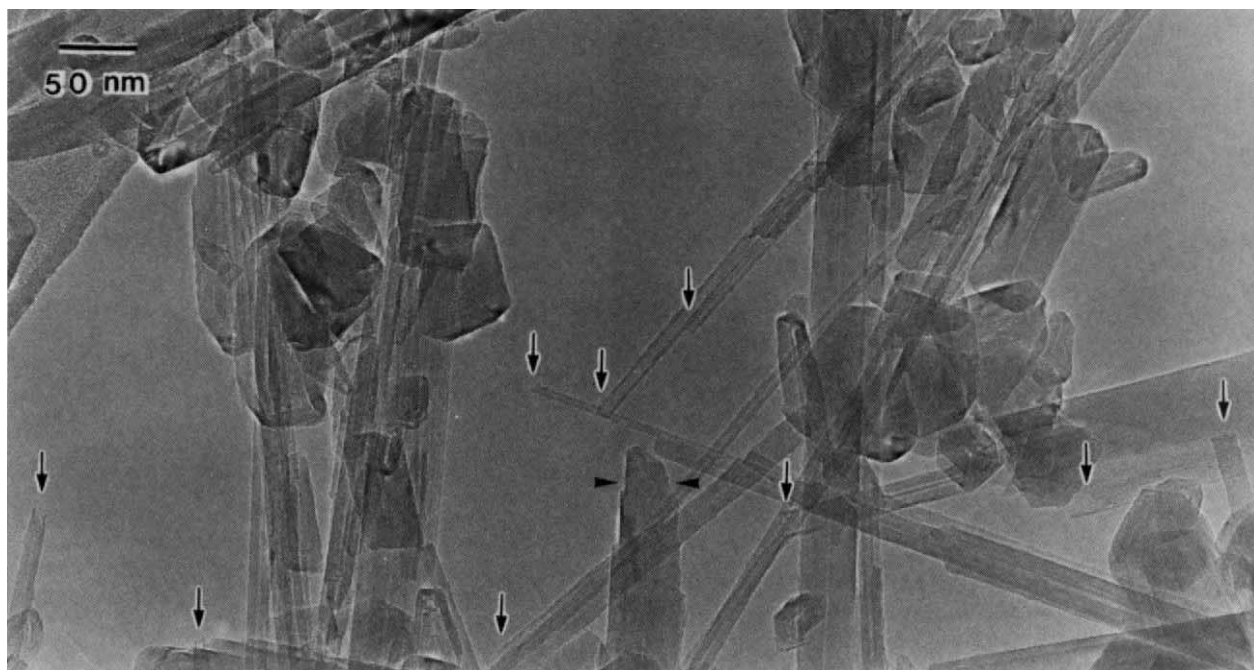


FIG. 2 Low-magnification transmission electron micrograph showing a mixture of carbon nanotubes and nanoparticles that has been heated in air at  $800^\circ\text{C}$  for 10 minutes. Vertical arrows show the tube tips that have become

open during annealing. Horizontal arrowheads show a large tube that is not completely open but has been eroded from the top and sides. Many large nanoparticles have survived.

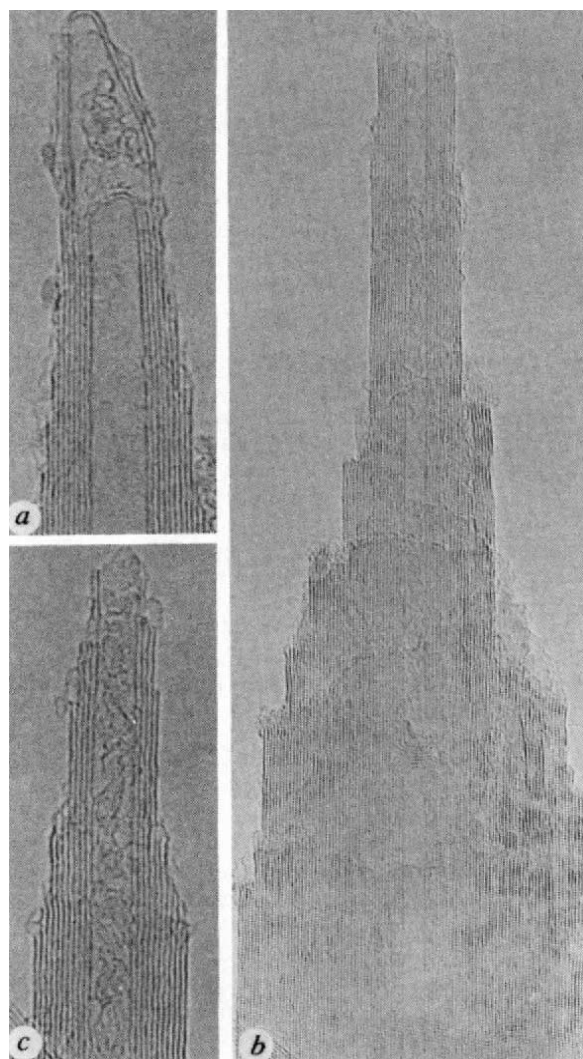


FIG. 3 High-resolution images of individual carbon nanotubes showing the structural damage that has occurred during oxidation in air. *a*, Conical tube which is not completely open but shows the removal of layers, starting from the cap region. *b*, Large tube which has been massively eroded at the edges. Shadows of the peripheries of outer, open tubes are seen clearly in the image. *c*, Opened tube showing carbonaceous debris that has been sucked into the inside hollow. Distance between fringes in the images is 0.34 nm.

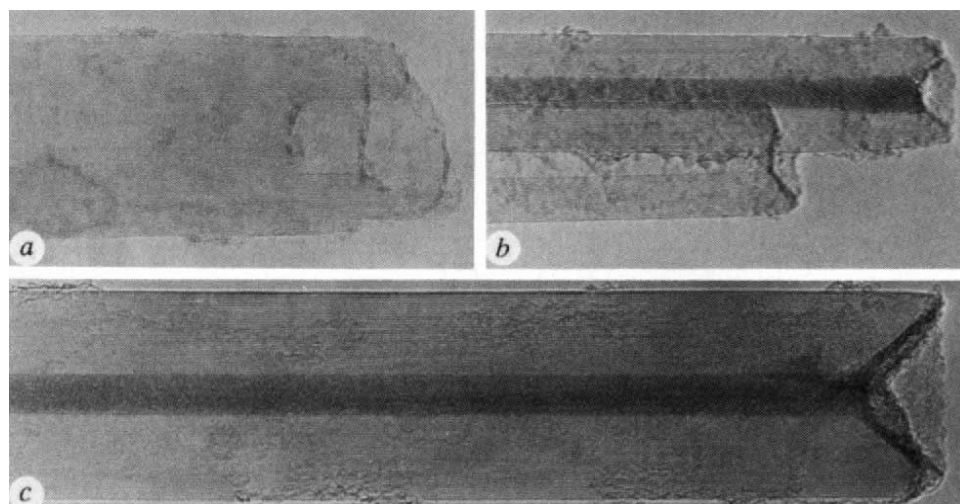
the metal oxide. We have also done experiments in pure oxygen (1 atm) but the reaction equilibrium was not shifted as much as when we used the oxide. Above  $\sim 750^\circ\text{C}$ , in pure oxygen, an ignition point is reached and sparks emerge from the sample.

Because the carbon nanotubes open readily in air at  $\sim 800^\circ\text{C}$ , it should be easy to introduce any oxides that are molten at or below this temperature. We have successfully filled the nanotubes with bismuth in the presence of oxygen by heating closed tubes with Bi metal in air at  $\sim 850^\circ\text{C}$  (Fig. 4c). The phase of the filling inside seems not to correspond to pure Bi metal (on the grounds of image and contrast). The weight loss of the sample when heated with Bi metal was much lower than expected, possibly because part of the oxygen supply in air was made available for the oxidation of Bi metal. Although it seems difficult to fill the inside cavities of already open tubes with pure metals by heating in vacuum, it might be possible to introduce unreactive metals such as gold by carefully controlling the partial pressure of oxygen (shifting the oxidation reaction equilibrium to higher temperatures) during the heat treatment. It should be easier for fluids and other low-viscosity materials to enter the tubes. Preliminary results show that it is possible to introduce Pt particles prepared in solution from dissolved  $\text{K}_2(\text{PtCl}_4)$  into some larger cavities of open tubes. It might be possible in future to perform catalysis or solution chemistry in the channels of open tubes and compare with experiments done outside.

It is clearly much easier to fill nanotubes in a one-step process from closed tubes than in a two-step process in which one first makes open tubes. The capillarity forces in the nanometre-sized cavities<sup>7</sup> may be adversely affected by contaminants sucked in during the opening process. During the filling process, capillarity forces compete with factors such as surface tension, the metal viscosity and so on. But how are these problems overcome when the nanotubes are filled in a one-step process from closed tubes? One possibility is that the inside cavities of the closed tubes are vacuum, or near-vacuum, and that when they are opened in the presence of the metals, the latter are sucked in. The chance of He or other inert gases being present inside the cavities of fullerenes is remote, as pointed out recently<sup>8</sup>, and this adds weight to our argument. The meaning of vacuum in such small cavities is unclear. A simple estimate shows that only about 20 gas molecules would be found in a  $1\text{-}\mu\text{m}$ -long,  $10\text{ \AA}$  hollow tube at 1 atm pressure, assuming no adsorption. In such small domains the description of usual physical quantities such as pressure and surface tension is not obvious<sup>9</sup>.

The availability of open tubes not only leads to new physics but should also open the possibility of interesting chemical

FIG. 4 Images showing filling of tubes. Separation between two parallel fringes is 0.34 nm. *a*, Open tube that has been heated with lead in Ar gas. No filling is seen but the periphery of the open end is seen decorated to be with, probably, the metallic phase. *b*, Filling of a lead phase inside a nanotube when closed tubes are heated with red lead in Ar. *c*, Filled nanotube with a bismuth phase filling.



catalysis, one-dimensional chemistry and perhaps even chiral chemistry. Tubular structures are also found in nature, so they might be used in biomimetic systems. As fluids should be able to move freely through the open ends of the tubes, physical phenomena involving constrained equilibrium due to strong capillary effects (such as the behaviour of superfluids) may be tested in the future. □

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## Continuous anchoring transition in liquid crystals

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**THE search for new ways of aligning liquid crystals<sup>1</sup> is motivated by their potential for optical and optoelectronic device applications. Rubbing of surfaces coated with an ‘aligning agent’ can induce an orientational preference in adjacent liquid-crystal films. Most of these surface preparations produce strong anchoring, in which the alignment remains pinned to the surface-induced orientation. But it is expected that for weak interactions with the surface, anchoring transitions may be possible in which the liquid-crystal orientation can be changed continuously, as a function of temperature for example<sup>2</sup>. Here we show that an anchoring transition can be observed for liquid crystals in contact with fluoropolymers as aligning agents. We find that the phenomenon might be general, and suggest that it provides the possibility of controlling precisely the angle of liquid-crystal alignment, and a method of producing weak anchoring.**

It is well known that weak surface forces can be used to orient liquid crystals<sup>1</sup>. A simple process of rubbing a glass plate with a piece of cloth in a given direction forces the liquid-crystal molecules to orient in the direction of rubbing. Although there continues to be some debate about the mechanism of alignment<sup>3</sup>, it is clear that at least in certain cases where the surfaces are coated with stretchable polymers, the alignment is due to the physical orientation of the polymer chains during the process of rubbing<sup>4</sup>. This oriented polymer then induces orientation of the molecules by pseudo-epitaxy; non-mesogenic materials such as polymers<sup>5</sup> may also be aligned in this way. This type of ordering, in which the orientation of the molecules is in the plane of the substrate, is often referred to as planar or homogeneous alignment. In another type of ordering, called homeotropic alignment, the director forms an angle of 90° with the surface plane. This arrangement can be produced by coating the surface with certain surfactants.

Most aligning materials produce one type of alignment or the other and although small deviations from 0° or 90° are possible, any arbitrary value between these values is generally difficult to achieve<sup>6</sup>. In some systems, however, the angle that the director makes with respect to the surface plane is temperature-dependent, and therefore in principle both types of alignment can be produced as a function of temperature. Ryschenkow and Kleman<sup>7</sup> were able to observe anchoring transitions of the nematic liquid crystal methoxybenzylidene butylamine (MBBA). By observing defects in these samples they were able to estimate the anchoring energy, and to show that these structural transitions were related to low anchoring energies. This observation has never been repeated or improved, and it has not been clear whether this is a unique system or whether other liquid crystals might exhibit similar behaviour.

A 0.05–2% solution of Fluorad 431 in ethanol or isopropanol was deposited on indium-tin-oxide-coated glass by a conventional spinning process, then dried at ~120 °C for varying times ranging from 30 minutes to ~24 hours. The typical thickness of the polymer layer was estimated to be 300–3,000 Å. Some plates were then rubbed to produce uniform in-plane orientation of the director, and the sample cells were made by using fibre spacers of the appropriate thickness, typically ~10 μm. This was deliberately chosen so that if the surface anchoring is weak, one should be able to observe wall defects whose width is  $\sim\sqrt{hK/W}$ , where  $K$  is the elastic constant,  $h$  is the sample

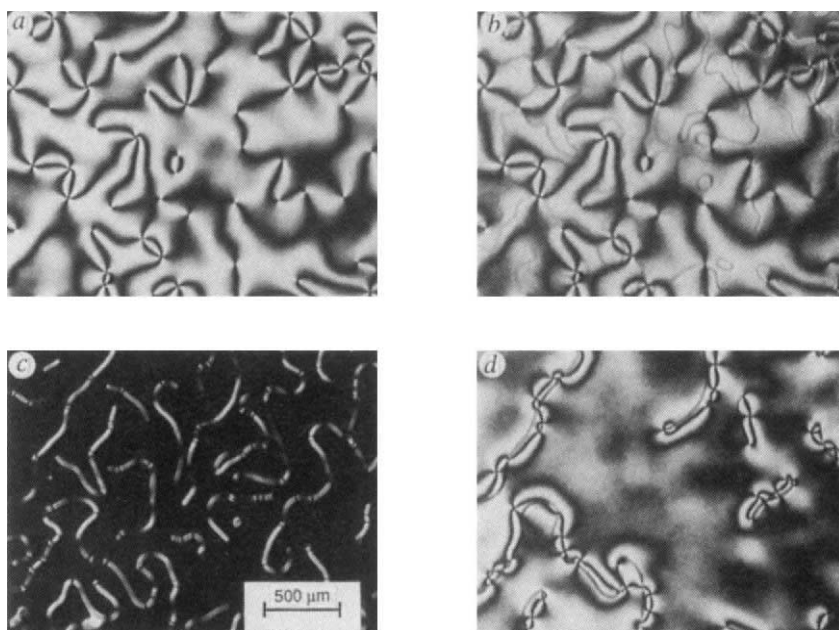


FIG. 1 Micrographs of a sample of liquid crystal at various temperatures. The sample was contained in a cell coated with fluorosurfactant and placed between cross-polarizers. The liquid crystal was E7 and the temperatures are (a) 40 °C, (b) 45 °C, (c) 55 °C and (d) 57 °C. All micrographs are at the same magnification.